

Characterization and technological behavior of basalt raw materials for Portland cement clinker production

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Abstract

This paper aims to characterize basaltic rocks as alternative raw materials for Portland cement clinker production and evaluate its possible use as an addition for the cement industry. It describes the physical, chemical and micro-structural characterization of the basalt clinker as well as the effect of its addition to Portland cements on the hydration, water demand, setting and mechanical strength of standardized mortars. The basalt blends may be used successfully as an aluminum silicate raw material for partial substitution of the conventional raw materials, leading to resources conservation and ensuring the quality of the produced cement. Investigating the use of basalts together with limestones materials may be essential in terms of the Cement Technology. Basalts blend decreases specific gravity of cements. Compressive strength test results of basalt blended cements indicated that basalt reacted with elements present in the medium in long term and also increased the strength values. The research reported in this manuscript demonstrates the potential of using basaltic rocks as a feedstock replacement in conventional Portland cement manufacture. It was shown that kiln operational conditions may have to be adjusted depending upon the quartz content of the basalts. The potential of this technology to contribute significantly to the sustainable management of basalt rocks were demonstrated by virtue of the annual volume of material consumable and the apparent technical feasibility of the approach.

Keywords: Basalt, limestone, cement industry, El-Yahmum, Naqb Ghul, Ghribun, Um Rihyat and Egypt.

1- Introduction

Cement is a manufactured product made by blending different raw materials and firing them at a high temperature in order to achieve precise chemical proportions of lime, silica, alumina and iron in the finished product, known as cement clinker. Cement is therefore essentially a mixture of calcium silicates and smaller amounts of calcium aluminates that react with water and cause the cement to set. The requirement for calcium is met by using high calcium limestone (or its equivalent calcareous raw material) and clay, mudstone or shale as the source of most of the silica and alumina. Finished cement is produced by finely grinding together around 95% cement clinker with 5% gypsum (or anhydrite) which helps to retard the setting time of cement.

Portland cement systems are often exposed to severe environments, and their long-term performance is of concern. The main results of a comprehensive investigation of deterioration processes that may affect the behavior of Portland cement systems exposed to chemically aggressive environments is presented.

In Portland cement manufacture, a mixture of limestone, shale, clay and sand are combined in controlled proportions and ground together either as a dry blend or water slurry. The ground mixture enters the upper end of the rotary kiln and moves down the kiln toward the burner zone. At high temperature, kiln charge reaches fusion temperature and small-size balls called clinker and also, fine solid particles of the raw material and semi-finish dust are formed (**Kerter, 1971**).

Rate of various reaction types influence by temperature (Kerter, 1971).

- 100- 500°C Dried and evaporated of the raw mixed materials
- 500-600°C Dehydroxylation of clay

$$2\text{SiO}_2 \text{ Al}_2\text{O}_3 \cdot 2\text{H}_2\text{O} \rightarrow 2\text{SiO}_2 + \text{Al}_2\text{O}_3 + 2\text{H}_2\text{O}\uparrow$$
- 700°C Activation of the silicates and removal of water
- 700-900°C Decarbonation of the calcium carbonate with initial combination of the alumina, ferric oxide
- 900-1200°C Belite form $2\text{CaCO}_3 + \text{SiO}_2 \rightarrow \text{C}_2\text{S} + \text{CO}_2\uparrow$
- >1250°C Formation of liquid phase (aluminate and ferrite)
- 1300°C The liquid phase appears and reaction C₂S with CaO to form C₃S.
- 1450°C Completion of reaction, alite and belite increase in size while free lime present in many area.

Chemical transformations during the thermal treatment of Portland cement raw meal (**Knöfel, 1977**).

- | Temperature °C | |
|----------------|---|
| <200 | Escape of free water (drying) |
| 100-400 | Escape of adsorbed water |
| 400 -750 | Decomposition of clay |
| 600 -900 | Decomposition of metakaoline and other compounds, with formation of a reactive oxide mixture. |
| 600 -1000 | Decomposition of limestone with information of CS and CA. |
| 800 -1300 | Uptake of lime by CS and CA, formation of C ₄ AF. |
| 1250 -1450 | Further uptake of lime by C ₂ S+C→C ₃ S. |

This paper presents a laboratory scale simulation that aims to investigate the possibility of partially substituting ordinary cement raw mix with basalt cement raw mix (BCRM), originated from a El-Yahmum and Naqb Ghul in North Eastern Desert, Egypt, in Portland cement clinker production. These raw mixed materials consist essential of two components calcareous and basalts.

The use of basalts instead of shales in cement industry was investigated by (**Hassaan 2001**). He recorded that basalt is a typical raw material for cement industry with little addition of sand to adjust the silica content to substitute shale in producing Portland cement clinker as a source of aluminum silicate. **Hassaan**

(2001) concluded that basalt is better than clay in cement clinker manufacture because it is more economic, since it saves the money of adding pyrite ash or any other iron compound to the raw mix in case of using clay. On the other hand, basalt rock has a density about twice that of clay, so the cost of transportation from the field to the factory will be about half that of clay. At the same time, the by-pass dust problem is expected to be diminished because the weight of the very fine grain of basalt is about twice that of clay of the same size.

El-Ashkar (2002) recommended that the basalt rock is typically raw material to replace clay, partially or totally, in producing Portland cement clinker. The advantages of using basalt instead of clay in cement clinker are summarized in the following points:-

1. New cement factories could be established of different localities at which shales is not available.
2. Basalt is economic in cement production, since it saves the money of adding either iron compound (pyrite ash) or sand to compensate the lack of the iron and silica content in the raw mixture of the clinkerization process.
3. Basalt rock has a density equal to about twice that of clay this means that basalt saves half of the cost of the transportation of the clay from the field to the factory.
4. The bypass dust problem in cement factories is expected to be diminished because the sulphate content in basalt is neglected in comparison with clay.
5. The relative high percentage of iron oxide in basalt makes the heat of formation of the clinker become lower.
6. The relative high content of magnesium oxide in basalt could be avoided by using limestone of low magnesium oxide content.

Calcareous component supplies the major portion of lime (calcium) which proved types of the limestone, and marly limestone and represented by alkali component. Argillaceous component supplies the major portion silica, alumina and ferric which extracted from basalts raw materials and represented by acidic component.

The raw materials of two components calcareous and basalts are main materials of the clinker cement which extraction from quarrying of the limestone and basalt rocks. Chemical analysis and parameter of the predominant oxides to estimation for these materials after known of the convention of the cement clinker manufacture. Portland cement is prepared by firing a mixture of raw materials: one of which is mainly composed of calcium carbonate and the other of aluminum silicates (**Lea, 1970**).

The use of basalt as alternative raw materials in cement industry that can be used as source of aluminum silicate, in order to improve the burnability of the raw mix and the effect of minor components on the formation of the clinker.

2- Experimental procedure

2.1. Material investigation

Basalts and limestones used in this investigation were collected from the El-Yahmum, Naqb Ghul, Gabal Ghribun and Um Rihyat areas in the north Eastern province of Egypt (**El-Desoky *et al.*, 2015**). The cement used was a locally manufactured ASTM at the laboratories of Qattamiya Cement Plant (QCP) and Tourah Cement Plant (TCP).

Chemical and physical properties of basalts and limestones are compared with those of (QCP) and (TCP) in **Table 1**. Chemical analysis indicated that basalts and limestones have very similar compositions and are principally composed of silica (about 50%) while the main components of limestones are calcium oxide. Both basalts and limestones have compounds like calcium oxide, alumina and iron oxide. The amount of oxides of sodium and potassium known as “alkalis” is found to be lower in basalts (3.55%; El-Yahmum or 3.41 %; Naqb Ghul) and limestones (0.21%; Um Rihyat or 0.19%; Gabal Ghribun) than that in cement (2.6% maximum, **El-Desoky *et al.*, 2015**).

Chemical analysis of the basaltic and carbonate rocks of the samples collected from the different localities in the study area where the major oxides data were obtained by using the X-Ray Fluorescence technique (**Table 1**). These analyses were carried out at the laboratories of **Qattamiya Cement Plant** and **Tourah Cement Plant**.

2.2. Basalts and limestones as cement raw mix

The preparation of limestone and basaltic samples for XRF analyses comprised:-

- 1- Crushing and milling to -200 mesh.
- 2- Preparation of pressed powder fused glass discs for major element oxides analysis using lithium tetraborate as a flux.

The chemical analyses were to determine the major chemical components of the raw mix for preparation of the clinker cement manufacture in the laboratories. Calculation and corrected of the average content and determination of the percentage of the major components of the raw mix from limestone and basaltic rocks to mode the clinker cement specimens according to **ES 4756-1 & EN 197-1 Standard** (ES: Egyptian Specification – EN: Egyptian Norm).

All samples were fused bead, placed in a Pt-dish and were thermally treated at 1450°C for 20 min in a muffle furnace and then were rapidly cooled. Sintering and cooling conditions were kept strictly constant (**Gebauer, 1978**).

The sintering reactions in all modified raw mix samples were recorded by means of differential thermal analysis instrument. The temperature was raised at a constant rate (10°C/min) from ambient to 1450°C. The experiments were conducted in a static atmosphere. The effect on the burnability was evaluated on the basis of the unreacted lime content in samples sintered at the above-

mentioned temperatures. The sintered pellets were ground and analyzed by the ethylene glycol method in order to estimate the free CaO (fCaO) content in the final sintering products and using a Siemens D-5000 X-Ray Diffractometer, with nickel-filtered CuK α 1 radiation ($k = 1.5405\text{\AA}$), in order to identify the mineralogical phases formed during sintering.

2.3. Preparation of raw mix cement clinker

The raw mix for the production of cement clinker comprises calcareous and basalt materials. The basalt raw material is a source of both aluminum and silica. It may contain one or more types of silicate minerals. Other sources of silica are quartz, sand, chalcedony, opal and feldspar. They are characterized by techniques such as DTA, XRD, SEM, and chemical analysis. The chemical compositions of materials used in the experiments are presented in [Table 1](#).

Four different types of cement raw mix were used in this study: Two types of basalts were manually collected from ten individual samples of El-Yahmum and Naqb Ghul represented by basaltic rocks which provided to silica (SiO $_2$), aluminum (Al $_2$ O $_3$) and iron oxide (Fe $_2$ O $_3$), and two sections collected from Gabal Ghribun and Gabal Um Rihyat represented by calcareous materials included limestone rocks which provided calcium carbonate (CaCO $_3$).

The samples were mixed very well by using a mixer. This procedure was carried out many times. The samples from four processes were sieved through a 300-mesh-sieve.

After the application of strengths and setting time tests to the cement mortars, X-ray diffraction and SEM analysis were applied to the mortar samples in order to determine the hydration products which formed during the hydration of the cement. SEM and X-ray specimens (w/c: 0.30) were put in glass bottles, the taps tightly closed, and aged for 28 days at the constant temperature (20°C). SEM micrographs of the surface of specific samples were taken by Leitz AMR-1000 SEM by covering them with golden films under 0.2 mmHg pressure in argon atmosphere. X-ray diffraction analyses were carried out by AXios- X-ray diffractometer.

Scanning electron microscopy was used in selected samples in order to examine the texture of the obtained clinkers at 1450°C and the distribution of the foreign elements in their main phases. A JEOL JSM-5600 scanning electron microscope, interfaced to an OXFORD LINK ISIS 300 energy dispersive X-ray spectrometer (EDXS) was used. Experimental conditions involved 20 kV accelerating voltage and 0.5 nA beam current.

Table 1. The chemical composition of the cement raw mix materials.

Oxides	BH	BN	LR	LG
SiO ₂	51.16	51.33	0.39	0.44
Al ₂ O ₃	14.34	14.72	0.10	0.16
Fe ₂ O ₃	12.80	12.10	0.08	0.08
CaO	9.45	10.16	54.93	55.14
MgO	5.79	5.08	0.38	0.31
SO ₃	0.02	0.04	0.20	0.06
K ₂ O	0.95	0.46	0.01	0.01
Na ₂ O	2.60	2.95	0.20	0.18
Cl	0.07	0.11	0.22	0.18
L.O.I	1.90	2.25	42.08	43.10
LSF	5.61	6.01	4352.61	3743.89
SR	1.89	1.91	2.17	1.83
AR	1.12	1.22	1.25	2.00

BH: El-Yahmum basalt.

BN: Naqb Ghul basalt.

LR: Um Rihyat limestone.

LG: Ghribun limestone.

2.4. Procedure and principles steps for the prepare clinker samples

The procedure and the principles steps to the prepare clinker samples from basalts instead shale with limestone rocks in laboratory as the following:-

1. The raw materials mixed which composed mainly of limestone and basalt.

2. The bulk of limestone and basalt crushed in either one or two stages by crushing machines special in the laboratory into fine powder (grinding) of the raw mixed by raw mill machines.

3. The chemical analysis, parameter factors for these raw mix and corrective by addition other materials to estimation elements oxides to suitable prepared of the raw meal after known of the convention of the cement clinker as the following:-

The main parameter factors affect in the raw meal:-

1- Lime saturation factor (LSF).

2- Silica ratio (SR).

3- Alumina ratio (AR).

Calculation of the lime saturation factor, silica ratio and alumina ratio from the data of the chemical analysis of the raw mix (RM) were listed in [Tables \(2-5\)](#). The chemical composition of each type of raw mix was obtained using X-ray fluorescence (XRF) and is presented in [Tables \(2 – 5\)](#). Ordinary Portland cement raw meal of industrial origin was used (residue at 90 μ m: 15%).

Limestone + basalt → raw mixed → crusher → Homogenized → grinding in raw mill and dryer → blend silo → Pre-heater → Kiln (sinter) →

cooler → pulverizing clinker + and added gypsum in cement mill → cement storage silos → packing.

Table 2. Show data of the chemical analyses, corrective and raw mix of El-Yahmum basalt (H) and Um Rihyat limestone (R).

	Basalt H	%	Limestone R	%	CC	%	RM
SiO ₂	51.16	19.50	0.39	72.50	41.39	8.00	13.57
Al ₂ O ₃	14.34	19.50	0.10	72.50	5.82	8.00	3.33
Fe ₂ O ₃	12.80	19.50	0.08	72.50	2.80	8.00	2.78
CaO	9.45	19.50	54.93	72.50	20.48	8.00	43.31
MgO	5.79	19.50	0.38	72.50	2.57	8.00	1.61
SO ₃	0.02	19.50	0.20	72.50	1.50	8.00	0.27
K ₂ O	0.95	19.50	0.01	72.50	1.26	8.00	0.29
Na ₂ O	2.60	19.50	0.20	72.50	0.79	8.00	0.72
Cl	0.07	19.50	0.22	72.50	0.21	8.00	0.19
LSF	5.61		4352.61		16.44		99.01
SR	1.89		2.17		4.80		2.22
AR	1.12		1.25		2.08		1.20

Table 3. Show data of the chemical analyses, corrective and raw mix of Naqb Ghul basalt (N) and Um Rihyat limestone (R).

	Basalt - N	%	Lime - R	%	CC	%	RM
SiO ₂	51.33	18.00	0.39	72.00	41.39	10.00	13.66
Al ₂ O ₃	14.72	18.00	0.10	72.00	5.82	10.00	3.30
Fe ₂ O ₃	12.10	18.00	0.08	72.00	2.80	10.00	2.52
CaO	10.16	18.00	54.93	72.00	20.48	10.00	43.43
MgO	5.08	18.00	0.38	72.00	2.57	10.00	1.45
SO ₃	0.04	18.00	0.20	72.00	1.50	10.00	0.30
K ₂ O	0.46	18.00	0.01	72.00	1.26	10.00	0.22
Na ₂ O	2.95	18.00	0.20	72.00	0.79	10.00	0.75
Cl	0.11	18.00	0.22	72.00	0.21	10.00	0.20
LSF	6.01		4352.61		16.44		99.19
SR	1.91		2.17		4.80		2.35
AR	1.22		1.25		2.08		1.31

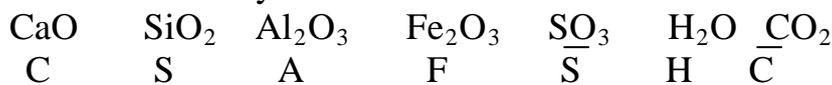
Table 4. Show data of the chemical analyses, corrective and raw mix of El-Yahmum basalt (H) and Ghribun limestone (G).

	Basalt H	%	Limestone G	%	CC	%	RM
SiO ₂	51.16	18.50	0.44	72.00	41.39	9.50	13.71
Al ₂ O ₃	14.34	18.50	0.16	72.00	5.82	9.50	3.32
Fe ₂ O ₃	12.80	18.50	0.08	72.00	2.80	9.50	2.69
CaO	9.45	18.50	55.14	72.00	20.48	9.50	43.39
MgO	5.79	18.50	0.31	72.00	2.57	9.50	1.54
SO ₃	0.02	18.50	0.06	72.00	1.50	9.50	0.19
K ₂ O	0.95	18.50	0.01	72.00	1.26	9.50	0.30
Na ₂ O	2.60	18.50	0.18	72.00	0.79	9.50	0.69
Cl	0.07	18.50	0.18	72.00	0.21	9.50	0.16
LSF	5.61		3743.89		16.44		98.48
SR	1.89		1.83		4.80		2.28
AR	1.12		2.00		2.08		1.23

Table 5. Show data of the chemical analyses, corrective and raw mix of the Naqb Ghul basalt (N) and Ghribun limestone (G).

	Basalt N	%	Limestone G	%	CC	%	RM
SiO ₂	51.33	18.00	0.44	72.00	41.39	10.00	13.70
Al ₂ O ₃	14.72	18.00	0.16	72.00	5.82	10.00	3.35
Fe ₂ O ₃	12.10	18.00	0.08	72.00	2.80	10.00	2.52
CaO	10.16	18.00	55.14	72.00	20.48	10.00	43.58
MgO	5.08	18.00	0.31	72.00	2.57	10.00	1.39
SO ₃	0.04	18.00	0.06	72.00	1.50	10.00	0.20
K ₂ O	0.46	18.00	0.01	72.00	1.26	10.00	0.22
Na ₂ O	2.95	18.00	0.18	72.00	0.79	10.00	0.74
Cl	0.11	18.00	0.18	72.00	0.21	10.00	0.17
LSF	6.01		3743.89		16.44		99.20
SR	1.91		1.83		4.80		2.34
AR	1.22		2.00		2.08		1.33

In the cement chemistry abbreviations shorthand are often used:-



3-Results and discussions

The clinker contains 4 major phases alite, belite, aluminate and ferrite (OPC: Ordinary Portland Cement).

Clinker chemistry:-

C3S (tricalcium silicate) → (35%-70%)

C2S (dicalcium silicate) → (15%-30%)

C3A (tricalcium aluminate) → (5%-10%)

C3AF (tetracalcium aluminoferrite) → (5%-10%)

The principle steps of the raw materials to forms clinker cement manufacture as the following (Basic cement manufacture).

3.1-Chemical Composition

Chemical elements of the cement clinker consist mainly of four components: calcium oxide (CaO), silicon oxide (SiO₂), aluminium oxide (Al₂O₃), iron oxide (Fe₂O₃).

The chemical reaction of the raw materials represented by limestone with basalts of the study area burning toward high temperature at about 1450°C in the special furnace in the laboratory to transforms into clinker which is ground together with about 5 % of gypsum to form Portland cement (Table 6).

Table 6. Chemical analysis of the limestone, clinker and raw mix.

Oxide	Limestone	Raw mix	Clinker (Wickert, 1984)
SiO ₂	1.9	14.3	22.2
Al ₂ O ₃	0.81	3.6	5.0
Fe ₂ O ₃	0.52	2.0	2.8
CaO	55.2	42.0	65.4
MgO	1.4	1.8	1.8
SO ₃	0.56	0.25	0.54
K ₂ O	0.22	0.63	0.63
Na ₂ O	0.08	0.22	0.25
TiO ₂	0.05	0.17	0.27
Mn ₂ O ₃	0.02	0.10	0.09
P ₂ O ₅	0.01	0.06	0.14
Cl	0.01	0.01	0.01
LOI	42.2	35.1	0.48

The chemical composition of the clinker contains some minor phases such as alkali, sulphates and calcium oxide. Raw mix constitutes four main oxides calcium, silica, aluminum and iron and minor non-volatiles such as SiO₂,

MgO, TiO₂, and MnO and also contains minor volatiles such as K₂O, Na₂O, SO₃, Cl and H₂O.

The cement clinker contains small amounts of alkalis and sulphate derived from raw materials and present in the major clinker phases such as the silicate, calcium and aluminatate.

Na₂SO₄ and K₂SO₄ accelerate the hydration of C3S and give rise to enhanced 2-days and 7-days strength but diminish the 28-days compressive strength. The degree of hydration decreases with increase of alkali oxide content. The increasing of SO₃% (about 1.86-0.65%) in clinker causing expansion of the concrete, slowing setting and reduction of strength where the strength decreases with increasing SO₃%. The higher alkalis (>1%) in clinker cause expansion of cement and reduce the compressive strength and high chloride also cause reduces the strength and form rust in the steel due to reaction between chloride (**Gebauer, 1978**).

The Portland cement samples are prepared by pulverizing the basaltic clinker specimens with small amount of the gypsum material in machine mill. The chemical analysis of the Portland cement samples is presented in **Table (7)**.

Table 7. Show the chemical analysis of the prepared cement samples from El-Yahmum and Naqb Ghul basalts (BH - BN) after grinding basaltic clinker with gypsum.

	BHG Cement	BHR Cement	BNG Cement	BNR Cement
SiO ₂	20.50	19.70	20.29	19.94
Al ₂ O ₃	5.7	6.00	5.43	5.05
Fe ₂ O ₃	4.22	4.71	4.50	4.25
CaO	62.33	61.90	62.19	62.18
MgO	2.10	2.38	2.49	2.30
SO ₃	2.70	2.69	3.02	2.91
K ₂ O	0.12	0.12	0.11	0.13
Na ₂ O	0.33	0.26	0.29	0.30
LOI	1.88	1.89	1.45	2.62
Total	99.88	99.40	99.65	99.77

3.2- SEM studies of the clinkers

The Scanning Electronic Microscopic (SEM) examine the texture of the clinker samples are useful information both minerals of the raw materials and the process of the clinker which reveal the alite crystals are discrete and hexagonal shape while belite crystals are rounded form and size crystals of the alite larger than belite and also reveal both alite and belite crystals embedded in the matrix (interstitial material). SEM studies were conducted in order to

examine the structure of selected clinkers obtained and the distribution of the foreign elements in their main phases.

The SEM is an important instrument for the study of cement clinker. Images study of clinker surface topography are used to examine grains size, shape and cracks surface features are obtained by SEM and XRD analysis to provides qualitative and quantitative elemental composition of the samples cement clinker basalt under investigated. The clinker cement samples which preformed from limestone and basaltic mixture can be SEM examined by using a fine electron beam. These beam scans over the clinker samples surface to obtain an optical image of the surface which magnification from 110 xs to 12000 xs.

The samples of the clinker can be examined carefully of the quality and compound by using the energy dispersive x-ray spectrometry technique (EDAX) to determine semi-quantitatively the chemical composition of the observed minerals in the samples (**Wickert, 1984**). The samples of the clinker cement basalt investigated in Naqb Ghul (BN) and El-Yahmum (BH) by scanning electron microscopy reveal the minerals and their habit are displayed in (**Figs.1-5**) respectively. The figuration of the samples BH and BN exhibiting the minerals of the clinker cement which consists mainly of alite, belite, aluminate and ferrite. These minerals are recognized by:-

Alite (tricalcium silicate, C3S) forms the bulk of a clinker (40-70%) and recognized by a hexagonal crystal habit and crystal sizes up to about 150 μm and the forms of the crystals faces may be reveal euhedral, subhedral or anhedral. elite (dicalcium silicate, C2S) is present in the bulk of a clinker (15-40 %), and recognized by crystal a rounded shape with crystal sizes between 5 - 40 μm . β -belite polymorph is abundant in clinkers (**Figs.1-5**).

Aluminate (tricalcium aluminate, C3A) is present in the a clinker about (1%-15%) crystal forms are exhibiting irregular to lath-like shape and sometimes reveal as cubic or orthorhombic forms with crystal sizes range between small 1-60 μm while ferrite (tetracalcium aluminoferrite, C4AF), is present in the clinker range from 1% to 18% with crystal habits as dendritic, prismatic, and massive. Both aluminates and ferrites exhibit variable reactivity with water. The ferrite and aluminate phases may occur between interstitial or matrix phases and appears to bind the silicate crystals (**Figs.1-5**).

The photos were selected to be representative as far as the size and the shape of alite and belite crystals are concerned. With the spot analysis of EDXS, the composition of the principal phases was analyzed at five to eight points. Owing to instrumental limitations, accuracy in analyses of the minute grains in the interstitial phases proves difficult to achieve. In any case, the comparison of the spot analysis in each clinker phase can lead to only qualitative indications concerning the distribution of the minor elements in the individual clinker compounds.

From [Figures 2, 4 & 5](#) it is concluded that the addition of the basalt blends results in variations in the appearance of both alite and belite crystals. Alite was developed in large compact crystals, which tend to appear more prismatic and angular in shape, in contrast to the slightly angular hexagonal outline of C3S grains in reference and 2, 3, 5 samples. Belite as well was uniformly distributed, forming bigger in size and rounded in shape crystals. The amount of interstitial matrix in all tested samples was generally adequate, having a fine-crystalline structure.

3.3- Mineralogical Composition of the studied clinkers

All samples sintered at 1450°C have the structure of a typical clinker. The dominant phases (alite, belite, calcium aluminate and ferrite) were well crystallized, giving peaks at the common 2θ values. The real clinker phases of the produced clinker identified by the aid of X-Ray Diffraction patterns (XRD). [Figures \(6 & 7\)](#) show the XRD charts of the studied clinker samples and [Tables \(8 & 9\)](#) show the clinker phases, polymorphic phases and their modifications of the different phases giving rise to expect the hydraulic properties (Mechanical and engineering properties, cement soundness and setting).

XRD chart of the basaltic clinker samples in two areas El-Yahmum (BH) and Naqb Ghul (BN) reveal some minerals of the clinker which performs from basalt materials instead clays with calcareous materials. The alite (C3S) is the dominant constituent of clinker with composition of tricalcium silicate (Ca_3SiO_5) modified in composition and crystal structure by incorporation of foreign ions such as MgO, Al_2O_3 and Fe_2O_3 .

Alite	(tricalcium silicate, C3S)	58%
Belite	(dicalcium silicate, C2S)	23%
Aluminate	(tricalcium aluminate, C3A)	9%
Ferrite	(tetracalcium aluminoferrite, C4AF)	7%
Periclase	MgO	1%
Arcanite	K_2SO_4	1%
Free lime	CaO	1%

Table 8. The average chemical composition of the real clinker minerals ([Wickert, 1984](#)).

	Alite	Belite	Aluminate	Ferrite
SiO ₂	24.5	31.3	3.9	2.5
Al ₂ O ₃	1.3	2.2	30.8	22.5
Fe ₂ O ₃	0.8	1.2	6.9	23.7
CaO	70.6	63.8	54.6	49.1
MgO	1.1	0.5	1.1	2.6
K ₂ O	0.1	0.9	2.0	0.2
Na ₂ O	0.1	0.3	0.5	0.1

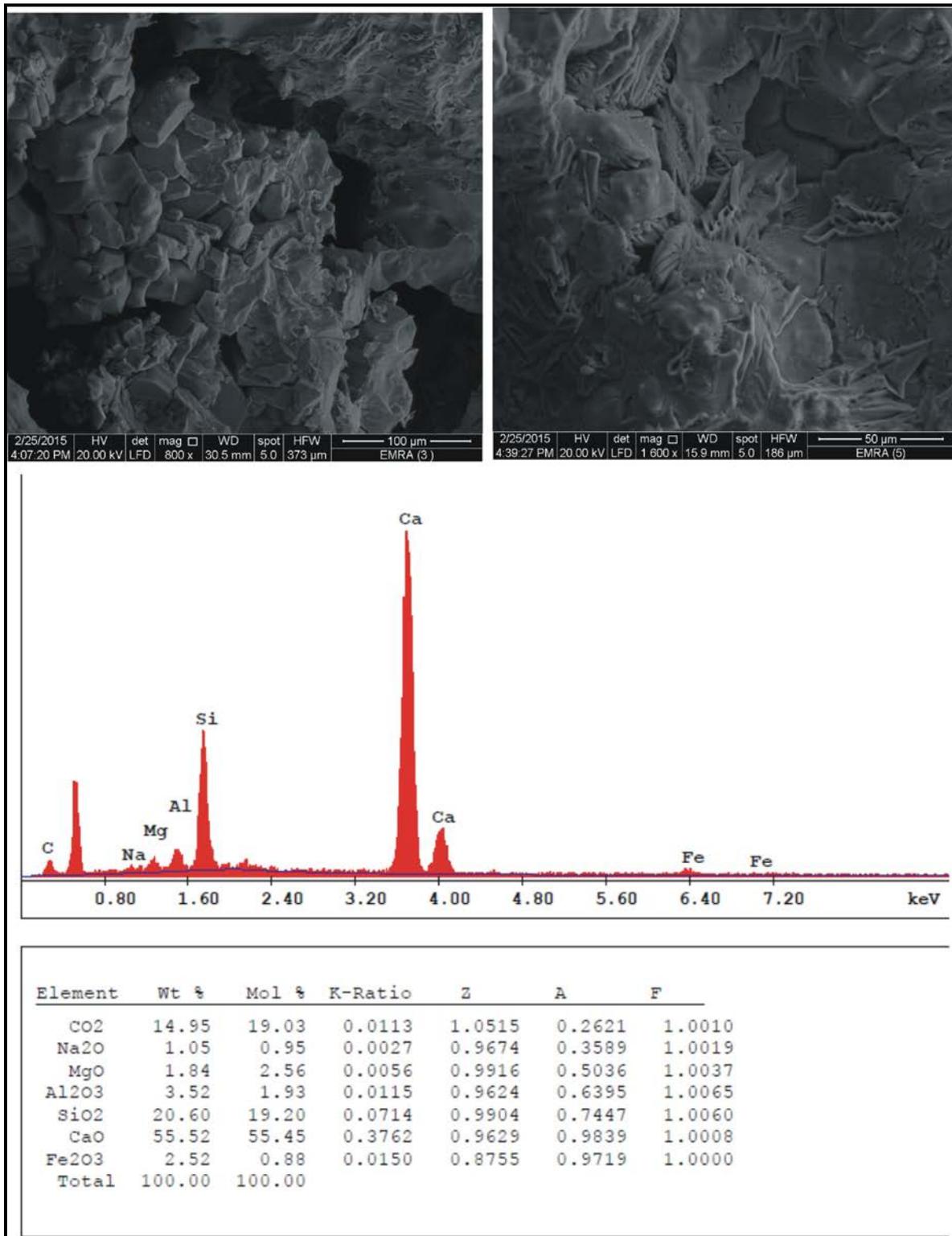


Fig.1. SEM image and EDX point analysis of El-Yahmum basaltic clinker.

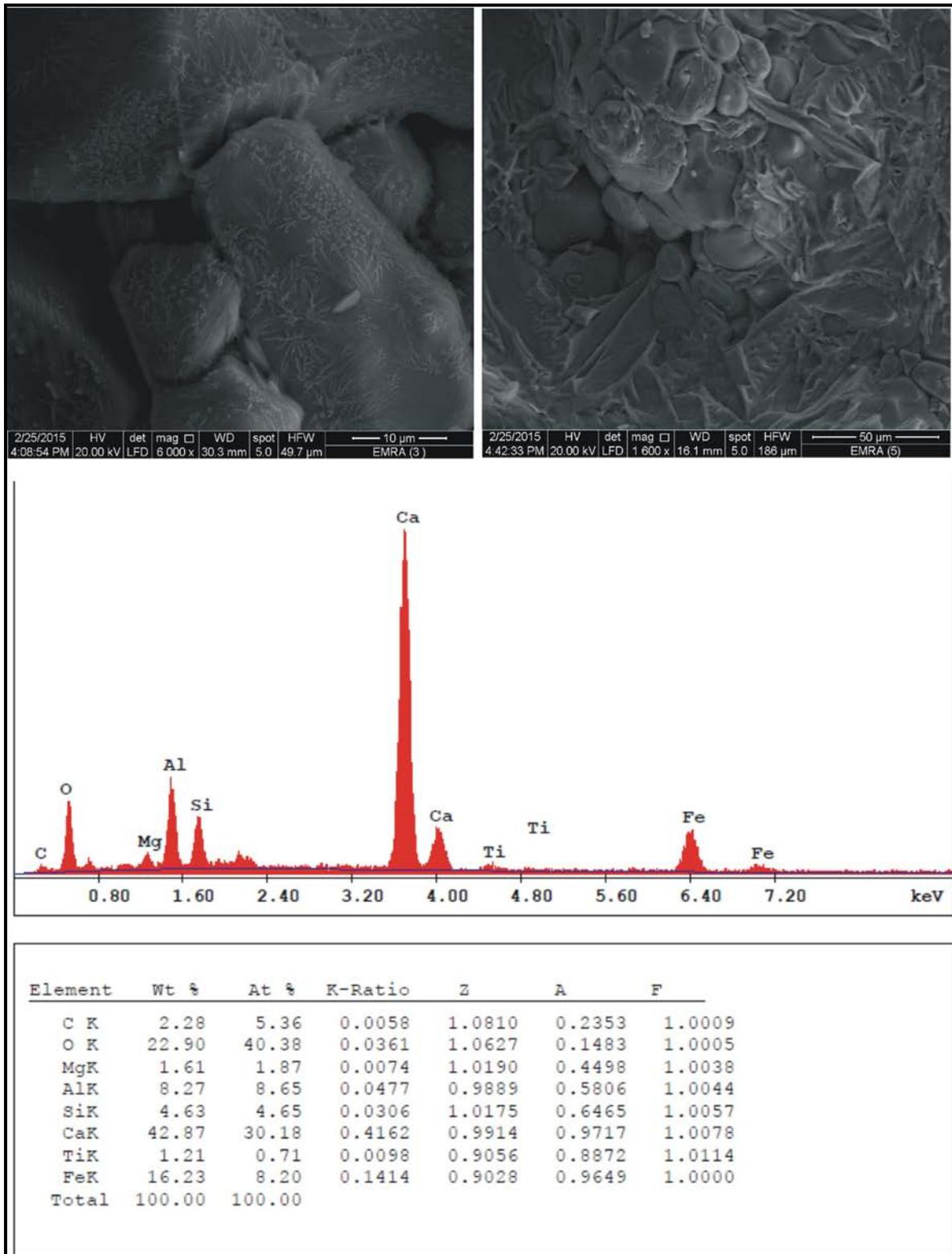


Fig.2. SEM image and EDX point analysis of El-Yahmum basaltic clinker.

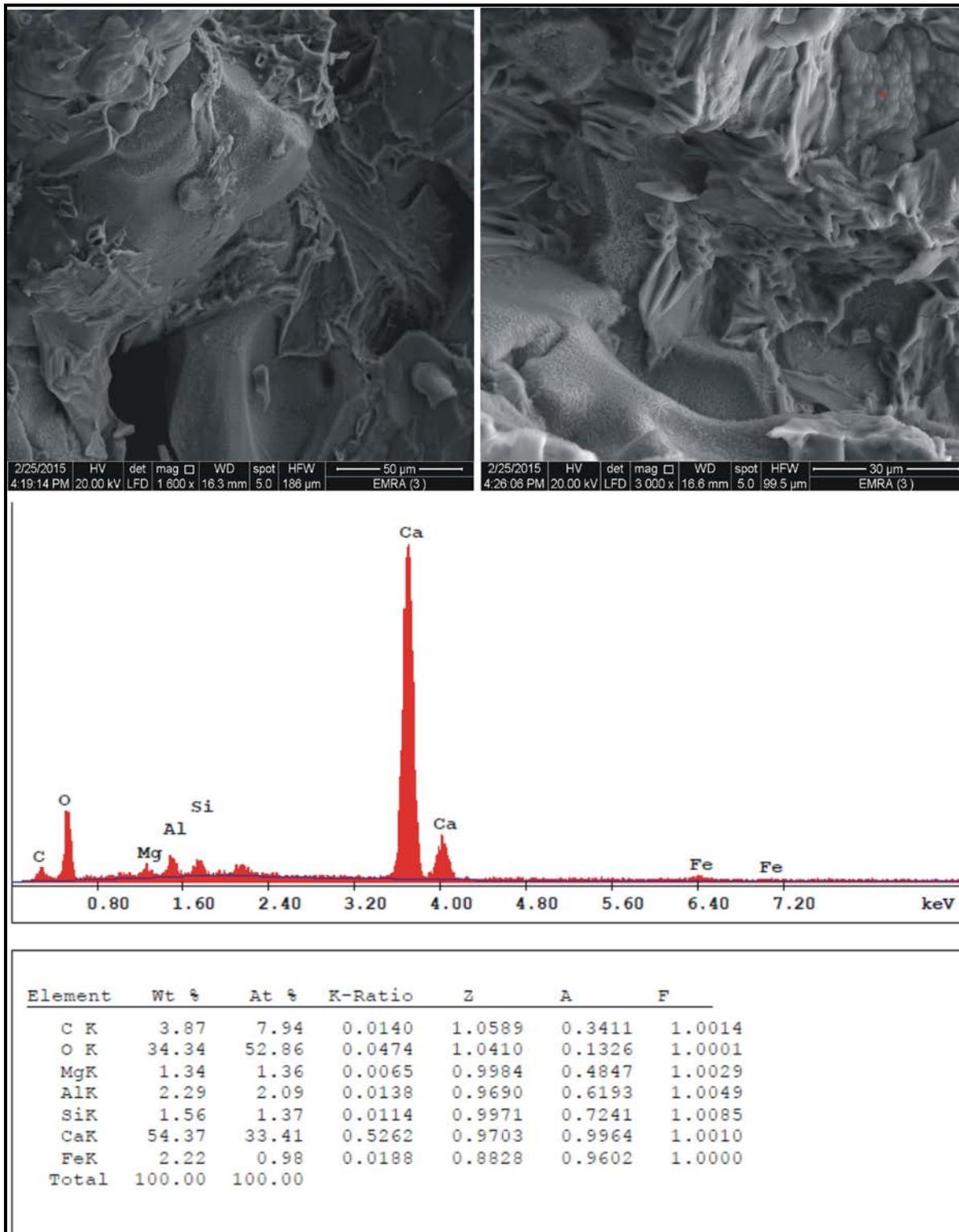


Fig.3. SEM image and EDX point analysis of El-Yahmum basaltic clinker.

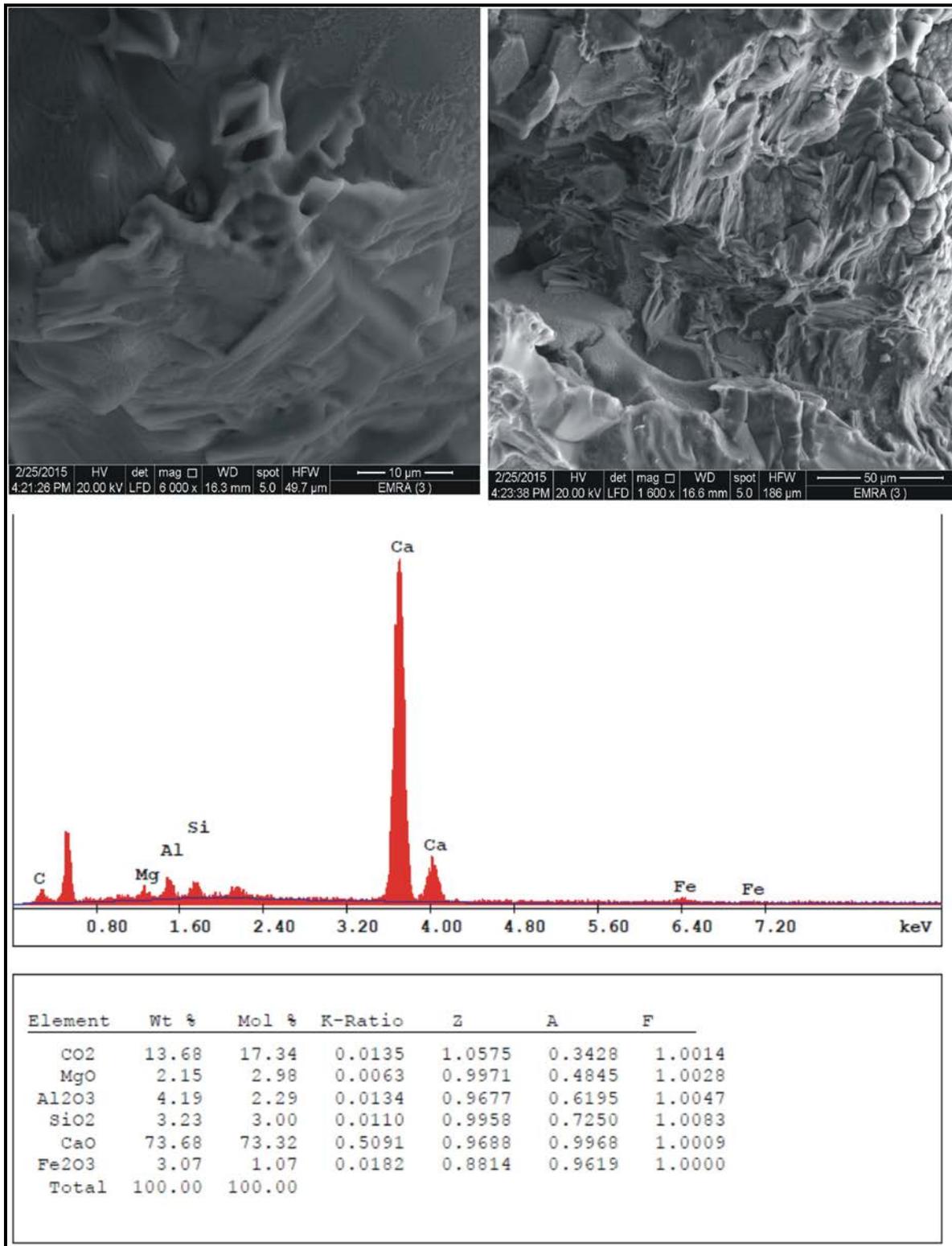


Fig.4. SEM image and EDX point analysis of El-Yahmum basaltic clinker.

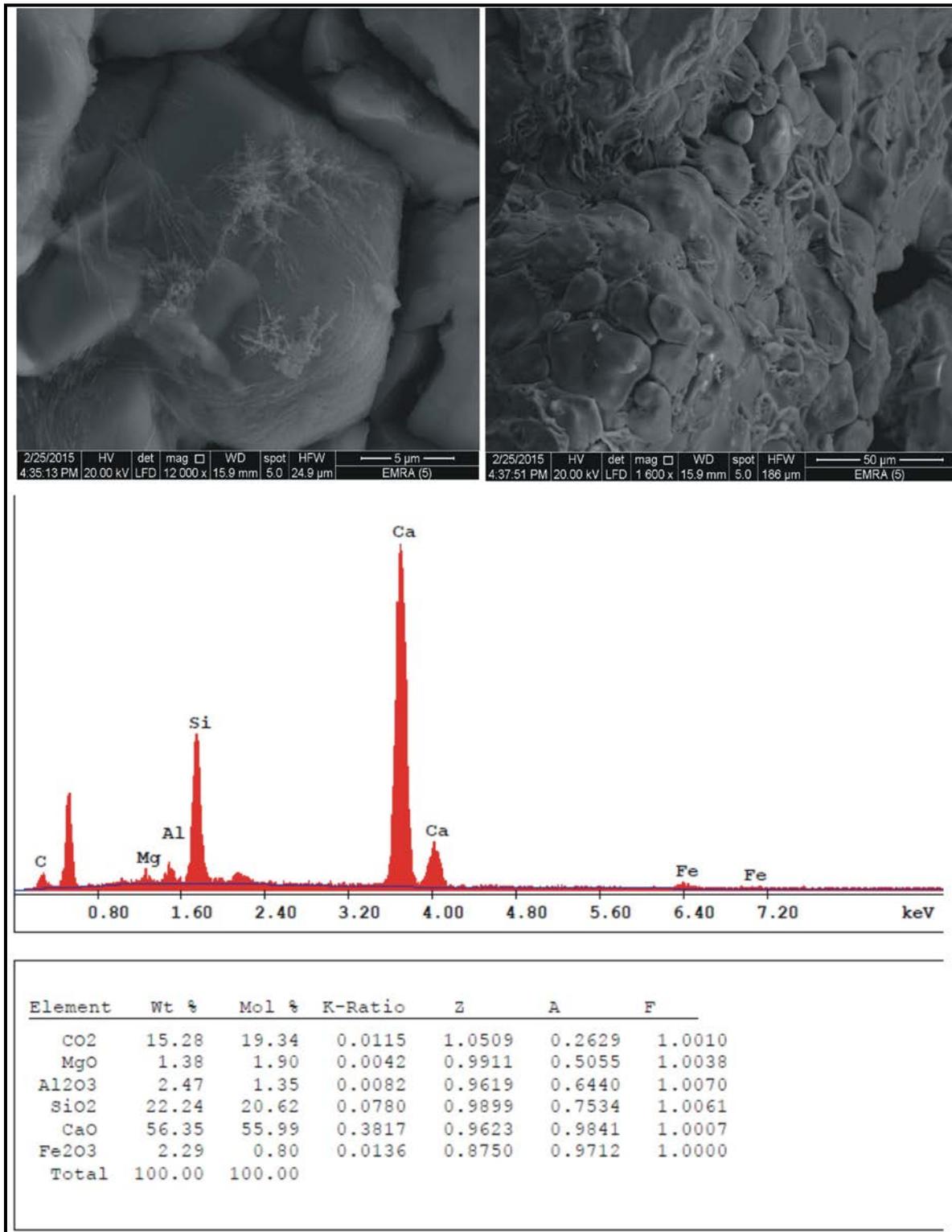
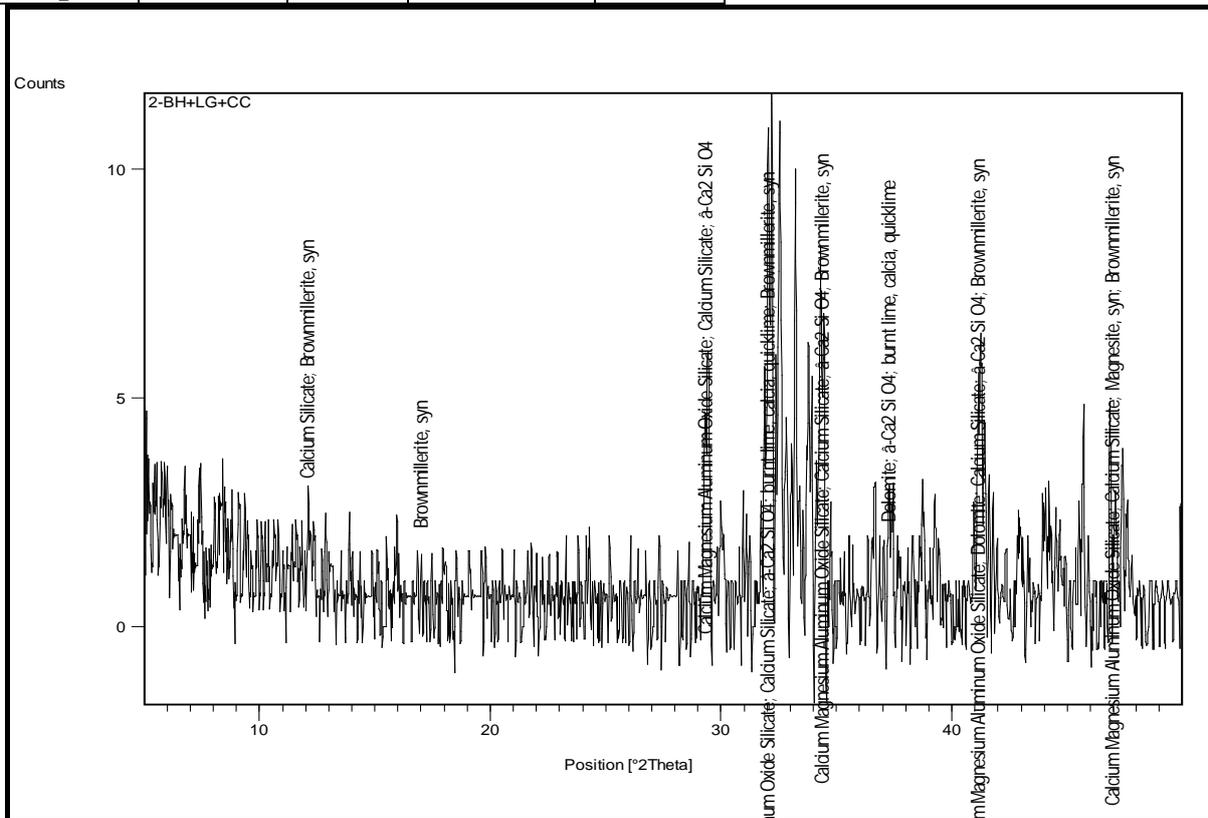


Fig.5. SEM image and EDX point analysis of Nuqb Ghul basaltic clinker.

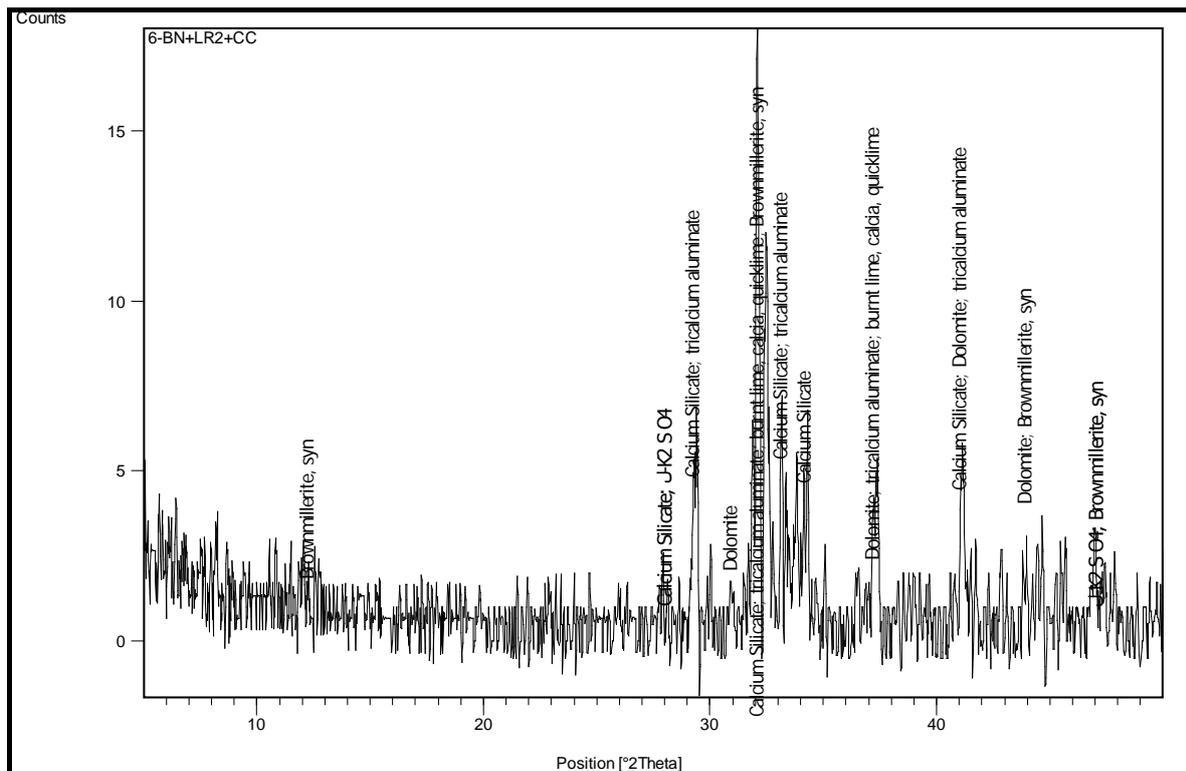
Table 9. Experimentally determined chemical composition of the clinker phases of a Portland cement clinker (**Knöfel, 1977**)

	Alite	Belite	Aluminate	Ferrite
SiO ₂	24.90	31.50	4.21	2.28
Al ₂ O ₃	1.12	1.84	27.52	19.60
Fe ₂ O ₃	0.64	0.96	5.76	22.52
CaO	69.70	63.20	59.50	51.40
MgO	0.89	0.48	0.85	3.18
K ₂ O	0.19	0.75	0.66	-



Compound Name	Chemical Formula
Calcium magnesium aluminum oxide silicate	Ca ₅₄ MgAl ₂ Si ₁₆ O ₉₀
Dolomite	CaMg(CO ₃) ₂
Calcium silicate	Ca ₃ SiO ₅
α-Ca ₂ SiO ₄	Ca ₂ SiO ₄
Magnesite, syn	MgCO ₃
burnt lime, calcia, quicklime	CaO
Brown millerite, syn	Ca ₂ (Al, Fe ⁺³) ₂ O ₅

Fig.6. Show XRD chart for the clinker synthetic minerals produced from basalt El-Yahmum.



Compound Name	Chemical Formula
Calcium Silicate	Ca ₃ SiO ₅
K ₂ SO ₄	K ₂ SO ₄
Dolomite	CaMg(CO ₃) ₂
tricalcium aluminate	Ca ₃ Al ₂ O ₆
burnt lime, calcia, quicklime	CaO
Brownmillerite, syn	Ca ₂ (Al, Fe ⁺³) ₂ O ₅

Fig.7. Show XRD chart for the clinker synthetic minerals produced from basalt Naqb Ghul.

The alite is detected by XRD in the clinker samples polymorphic form of the studied samples through the d-spacing 2.764Å the alite lines coincides with the lines of belite (β -C2S).

XRD chart of the clinker samples show the belite (C2S) is the second phase in intensity which identified from X-ray chart using lines at 2.76Å, 2.88 Å for α -C2S, 2.76Å - 2.69 Å for α - C2S while 2.77 Å, 2.74 Å, 2.607Å for β-C2S 3.002Å, 2.77Å and 1.98Å for δ-C2S.

The belite is predominant by β-C2S structure and highest hydraulic properties while the presence both α - C2S and α - C2S has been reported in all the basaltic clinker samples.

The aluminate phase (C3A) of the basaltic clinker has been identified from lines 2.70Å, 1.907Å and 1.566 Å.

The ferrite phase (C4AF) of the basaltic clinker which has been identified from X-ray chart using lines at 2.63Å, 2.77Å, 1.92Å and 7.24Å while C2F has been identified from X-ray chart using lines at 2.78Å, 2.63Å, 2.67Å and 1.94Å.

Free lime detected by XRD which has been identified from X-ray chart using lines at 2.778Å, 2.405Å, 2.67Å and 1.70Å while MgO (Periclase) has been identified from X-ray charts using lines at 2.106Å, 1.489Å and 1.70Å (Figs.6 & 7).

3.4- Thermal behaviour

Differential thermal analyses (DTA) can be applied to identify and evaluated the minerals of the clinker cement (raw mixed of the limestone with basaltic rocks) which can be differentiated by temperature at which the endothermic and exothermic peak occur.

Ferruginous minerals such as hematite, magnetite and siderite are characterized by fluxes of the melt and facilitate the clinkerization at lower temperatures. The burnability is affected by the chemical, granulometric and mineralogical compositions of the raw materials. The qualitative and quantitative of the C3S, C2S, C3A and C4AF minerals belonging to the clinker samples can be identifying by the application of DTA.

The application of DTA is assess the quality of the minerals clinker cement by identifying and evaluated the amounts C3S, C2S, C3A and C4AF. The application of DTA is also assess to determination several endothermal and exothermal peaks were obtained by the peak at 1250°C to formation alite and at 1175°C was attributed to the formation of belite while decarbonation occurred at about 650C.

The DTA differential thermal analysis data of the clinker from basaltic rocks appearance neglect variation of the endothermal peak at about 461C°-466C° in Naqb Ghul and El-Yahmum areas respectively (Figs. 8 & 9).

In the DTA curve of a cement raw mix the following stages are distinguished:-

- A broad endothermic effect attributed to the Dehydroxylation of amphiboles and chlorite (200–600°C),
- A strong endothermic effect around 900°C caused by the decomposition of the limestone,
- The endothermal effects at 900 and 976°C that are attributed to triclinic-monoclinic –trigonal transformations in C3S while C2S formation at 808°C,
- C4AF formation with exothermal peak at about 980-1000°C and C2F with an endothermal peak at 1160°C,
- The thermogram of the exothermal effects between 950-1000°C in the mix $\text{CaCO}_2 - \text{Al}_2\text{O}_3$ due to the formation of CA,
- In CaO and Fe_2O_3 (CF) system forms at about 950°C melting occurs at 1150°C which is reflected as an endothermal effect.

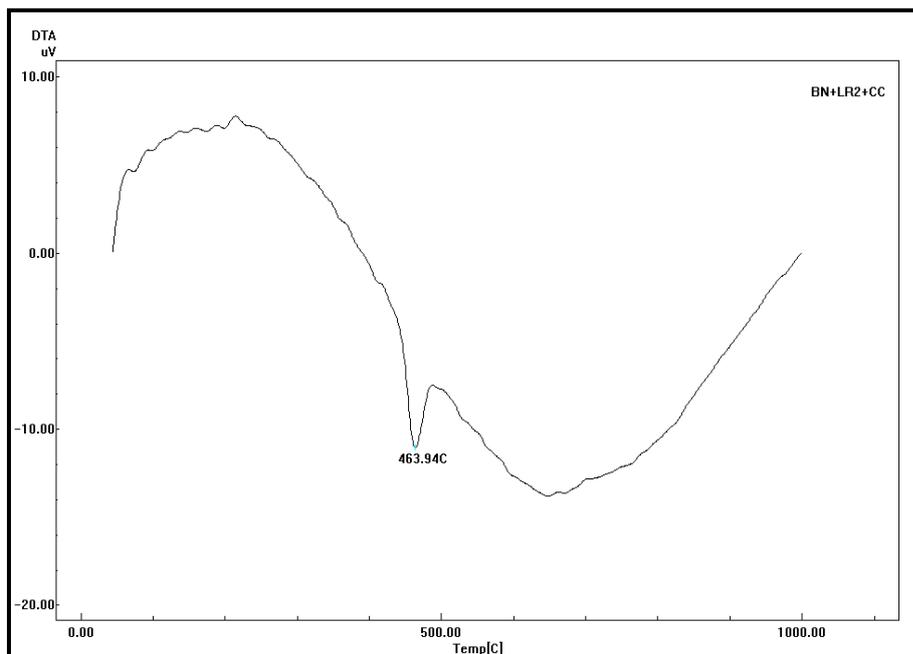


Fig.8. Show DTA curve of the clinker produced by using Naqb Ghul basalts.

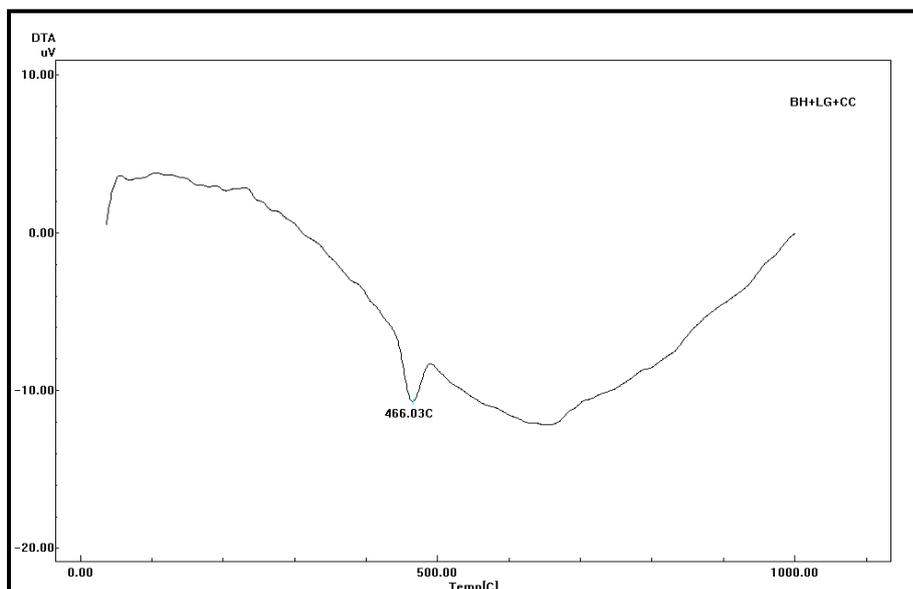


Fig.9. Show DTA curve of the clinker produced by using El Yahmum basalts.

The first two stages depend on the chemical and mineralogical characteristics of the basalt and the limestone respectively, and as it was expected, they are identical in all samples. The most important stages are the third and the fourth which are directly associated with the clinkerization process.

The evaluation of the DTA curves of all modified raw meals led to the following remarks:-

- In all modified samples the reactions associated with the decomposition of CaCO_3 (in the temperature range of 800–900°C) and clinkerization (1200–1450°C) are recorded, suggesting satisfactory burning and clinkerization of all samples.
- The added basalt blends do not affect the decomposition of CaCO_3 and the belite formation. In all modified mixtures the formation of the melt is shifted to lower temperature and overlapped with the belite formation. This fact indicates that the constituents of the added basalt blends are dissolved in the liquid phase, affecting mainly the formation and the properties of the melt and therefore change the reactivity of the mixture at high temperatures.

3.5- Chemical Parameters for Cement Materials

The main parameters controlling the chemical specification for raw mixed of the cement clinker which include three factors affected on the raw meal.

3.5.1- Lime Saturation factor (LSF)

$$\text{LSF} = \frac{\text{CaO}}{2.80 \text{ SiO}_2 + 1.18 \text{ Al}_2\text{O}_3 + 0.65 \text{ Fe}_2\text{O}_3}$$

Usual range in clinker: 95% – 100%

3.5.2- Silica Ratio (SR)

$$\text{SR} = \frac{\text{SiO}_2}{\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3}$$
 Usual range in clinker: **1.8% – 3.6%**

3.5.3- Alumina Ratio (AR)

$$\text{AR} = \frac{\text{Al}_2\text{O}_3}{\text{Fe}_2\text{O}_3}$$
 Usual range in clinker: **1% – 3%**

The high **LSF** values cause hard burning, an increase of C3S content due to slower setting, higher early strength and expansion of the cement due to form excess free lime while lower of LSF causes reduction of the early strength due to reduce C3S and increase C2S which increase the late strength ([Tables 10 & 11](#)).

The high silica ratio (SR) values cause hard burning of the raw mix, low liquid phase-increase in its viscosity and also cause washing of the coating and increase in the insoluble residue content ([Tables 10 & 11](#)).

Low SR with increase C3A and C4AF give rise to rapid setting cement and lower cement strength.

The high AR values increase the aluminate phase (C3A) and reduces the ferrite phase (C4AF) giving rise to rapid setting of the cement ([Tables 10 & 11](#)).

The cement made by finely pulverizing (grinding) of the clinker which produced by fusion a mixture of the calcareous and basalts materials in the present work.

3.5.4- Correctives

Some main elements of the raw mix of the cement clinker samples are insufficient proportion must be added as. These correctives may be:

Calcium provide (CaO)

Quartz provide (SiO_2)
 Bauxite provide (Al_2O_3)
 Pyrite ash or iron oxide provide (Fe_2O_3)

3.5.5- Additives

Some minerals grinding with clinker such as gypsum, slag, fly ash or pozzolans are added to improve Portland cement clinker. Chemical reaction transforms into clinker which is ground together with small amount of gypsum to form Portland cement.

3.6- Burning raw mixed

The burning zone parts of kiln model can be composed of four zones:-

3.6.1- Calcining zone

Decarbonation of kiln feed and form of the dicalcium silicate (C2S starts formation) which considerable exothermic and decarbonation needs heat

3.6.2- Heating zone-transition zone

The temperature of the material is between 900 –1300°C. The decarbonation is finished where the temperature is rises rapidly and intermediate phases takes place.

3.6.3- Liquid zone

Liquid phase is formed in between 1300 – 1350°C and begins of the tricalcium silicate (C3S) and nodulization of clinker and considerable the dominant process is the C3S growth.

This step is role play important for preparation of the clinker cement process where raw meal deals with gradually of the temperature in the kiln (Fig.10).

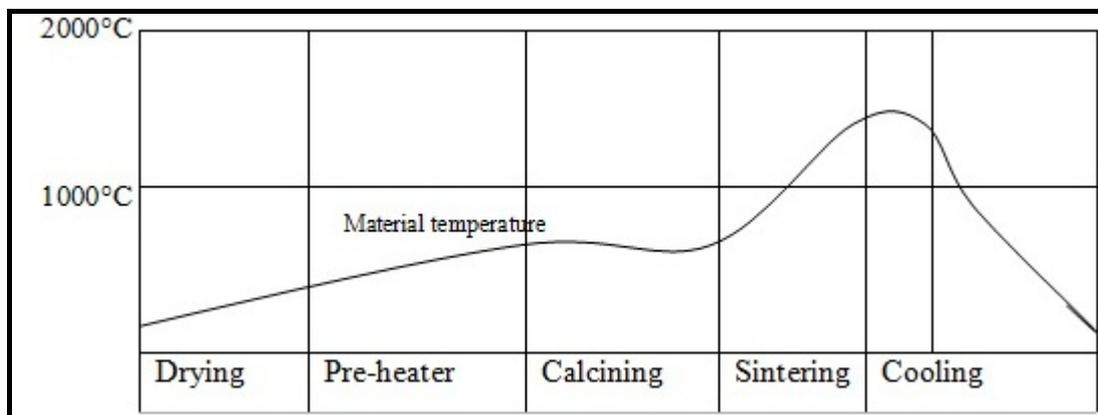


Fig.10. Showing the relationship between burning clinker process with gradually temperature.

In general some process functions of the basalt raw meal are performed in the furnace: Dry- heat- calcining-sinter and cooler zones respectively.

The basalt raw mixed of the clinker specimens placed in the machine to homogenization process after treatment by corrective materials and put in the furnace at about 100°C to evaporating of the water and complete dried process.

To preparation of the clinker cement start by dry process of the raw mix and transformation to completion clinker burning process in the furnace where raw meal deals with gradually of the temperature in the furnace start of the clinker burning (200-1450°C) to fusion a raw mixture of the calcareous and basaltic materials. The dry particles modified by dry process which transform clinker into nodules in the vicinity near of liquid phase.

Clinker burning involves transformation of natural mineral to a blend of synthetic minerals. The chemical reactions process of the burning cement clinker depending on gradually of the temperature and chemical composition of the raw materials. The chemical combinations of raw mix meal are decomposes and combines to form new chemical combination effected by high gradually temperature and form new minerals under very heat medium conditions.

Liquid phase is formed in between 1300–1350°C and begins of the tricalcium silicate (C3S) and nodulization of clinker.

Table 10. Show the chemical analyses and parameter of raw mix (RM) from basalt Naqb Ghul (BN) and limestone Ghribun (G) and corrective with the clinker by using shale at Qattamiya plants (QP), clinker by basalt and limestone (**Hassaan, 2001**), and standard of clinker by using shale in the world (**Hewlett, 1997**).

Oxides	BHG	BHR	BNG	BNR	QP	Hassaan, 2001	Hewlett, 1997
SiO ₂	20.00	19.80	20.71	20.61	21.32	21.5	21.70
Al ₂ O ₃	7.03	7.20	6.54	6.72	5.47	2.6	5.54
Fe ₂ O ₃	5.44	5.21	4.85	4.92	4.31	4.8	2.15
CaO	63.40	63.57	63.50	63.39	64.35	63.9	67.10
MgO	2.62	2.67	2.52	2.43	1.59	2.7	--
SO ₃	0.08	0.09	0.16	0.18	1.21	1.2	1.00
K ₂ O	0.02	0.03	0.06	0.05	0.27	--	--
Na ₂ O	0.26	0.24	0.32	0.31	0.50	--	--
Cl	0.01	0.01	0.01	0.01	0.014	--	--
LOI	0.38	0.37	0.42	0.45	0.36	--	--
Total	99.24	99.19	99.09	99.06	99.39	--	--
H.M	1.94	1.96	1.95	1.95	2.03	--	--
L.S.F	93.27	94.22	92.04	91.93	93.18	--	0.975
S.R	1.60	1.60	1.82	1.77	2.18	--	2.82
A.R	1.29	1.38	1.35	1.37	1.27	--	2.58
C3S	49.88	50.75	47.07	46.53	51.37	37.5	65
C2S	19.79	18.56	23.95	24.06	22.45	33.4	14
C3A	9.44	10.28	9.13	9.50	7.21	7.1	11.0
C4AF	16.54	15.84	14.74	14.94	13.10		6.5
BI	1.92	1.94	1.98	1.96	2.53		--

Table 11. Show data of the chemical analyses and parameter of raw mix (RM) basalt Naqb Ghul and limestone Ghribun and corrective with the clinker by using shale at Kawmiya plant (KP), and the clinker by using basalt at Qattamiya (QP) and Tourah (TP) plants and standard of clinker by using shale in the world.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14
	Basalt H	Basalt N	Limestone G	Limestone R	Standard	KP	RMG	RMR	Raw Mix	Clinker	Clinker BQ	Clinker BT	Clinker clay	Clinker Hassaan, 2001
SiO ₂	51.16	51.33	0.44	0.39	54.32	51.30	13.70	13.57	14.3	22.7	20.61	21.43	21.09	21.5
Al ₂ O ₃	14.34	14.72	0.16	0.10	16.15	18.75	3.35	3.33	3.6	5.7	6.72	5.81	4.80	2.6
Fe ₂ O ₃	12.80	12.10	0.08	0.08	9.30	11.04	2.52	2.78	2.0	1.9	4.92	4.24	3.50	4.8
CaO	9.45	10.16	55.14	54.93	2.01	3.44	43.58	43.31	42.0	66.0	63.39	62.83	64.65	63.9
MgO	5.79	5.08	0.31	0.38	2.25	2.44	1.39	1.61	1.8	2.0	2.43	2.37	2.31	2.7
SO ₃	0.02	0.04	0.06	0.20	0.26	1.05	0.20	0.27	0.25	0.33	0.18	0.32	1.21	1.2
K ₂ O	0.95	0.46	0.01	0.01	1.40	0.11	0.22	0.29	0.63	0.74	0.05	0.05	0.28	--
Na ₂ O	2.60	2.95	0.18	0.20	1.15	0.14	0.69	0.72	0.22	0.09	0.31	0.00	0.50	--
Cl	0.07	0.11	0.18	0.22	0.10	1.36	0.17	0.19	0.01	0.01	0.01	0.00	0.00	--
LSF	5.61	6.01	3743.89	4352.61	1.135	--	99.20	99.01	--	--	92.04	90.26	>95%	--
SR	1.89	1.91	1.83	2.17	5.61	--	2.34	2.22	--	--	1.77	2.13	2.35	--
AR	1.12	1.22	2.00	1.25	1.7	--	1.33	1.20	--	--	1.37	1.37	1.38	--
LOI	--	--	--	--	--	10.77	--	--	35.10	0.24	0.45	--	0.40	--

- 1-2: Chemical analyses of El-Yahmum (H) and Naqb Ghul (N) basalts.
- 2-3: Chemical analyses of Gabal Ghribun (G) and Um Rihyat (R) limestones.
- 5-6: Chemical analyses of the standard claystone and claystone at Kawmiya plant (KP).
- 7-8: Chemical analyses of the raw mix (RM) from Gabal Ghribun (G) and Um Rihyat (R) limestones mixed with El-Yahmum and Naqb Ghul basalts.
- 9-10: Chemical analyses of the raw mix (RM) and standard clinker.
- 11-12: Clinker chemical analyses of limestone mixed with El-Yahmum and Naqb Ghul basalts performed at Qattamiya (BQ) and Tora (BT) plants respectively.
- 13: Clinker chemical analysis of limestone mixed with claystone at Tora plant.
- 14: Clinker chemical analysis of clinker by basalt material according to **Hassaan (2001)**.

3.7- Physical and mechanical

The development of strength values is affected by the mineralogical structure of clinkers, pozzolanic reactions, Blaine and water demand as strength of cements is a function of the hydrated section (**Lea, 1970**). Clinker phases, which form the mineralogical structure of cements and which also have significant effects on strength values, are presented in **Table 13**. Strengths varied with proportional variation of clinker mineral phases depending on increasing blend ratios in all blended cement samples.

The basaltic clinker prepared by several steps in the laboratory to determine the compressive strength and cement setting times.

The Portland cement about 300g is mixed with about 26% water to form Portland cement paste and pouring in the mold cylinder (disk) and put in vessel (basin) water to measurement and determine initial and final of the setting time (**Table 12**).

The setting time data of the prepared cement specimens reveal initial setting time in the BH and BN are 175min. and 180min. respectively while finally setting time are 240min. and 242min. respectively. These data of the setting time refer to the Portland cement specimens are normal and suitable for the concrete.

The prepared cement (450 g) is mixed with sand (1350g) and 225ml water in the mixer machines to form mortar homogenization. The specimen mortar is pouring in the rectangular mould and then compact by vibrating machine and put in stored in circulating water at about 20°C and humidity 97 during 2days, 7days and 28 days. The specimens removed from water to measure a compressive strength by a compression machine according to the ES: 4756-1 & EN 197-1 Standard (CEM1 - 42.5N).

The compressive strength of the prepared cement specimens from basaltic clinker of the El-Yahmum and Naqb Ghul basaltic clinker (BH and BN) reveal that after 2-days and 7- days which appearance the compressive strength is normal. The compressive strength is 16.5N/mm² & 17.7 N/mm² after 2-days and is 27.08 N/mm² & 27.18 N/mm² after 7-days respectively. These compressive strength data of the prepared Portland cement raw mixed from basaltic clinker are suitable for concrete according to standard of ES: 4756-1& EN 197-1 Standard (CEM1- 42.5N) Standard (Table 13).

Table 12. Show setting time test of the prepared cement samples from grinding basaltic clinker with gypsum.

Set time	BHG	BHR	BNG	BNR	
Initial Min.	175	170	185	180	≥ 60 min.
Final Min.	235	230	245	240	< 10 hours

Table 13. Show the compressive strength data of the prepared cement samples from grinding basaltic clinker with gypsum.

Strength	BHG	BHR	BNG	BNR	
2 Days N/mm ²	16.35	16.50	17.50	17.90	10.0
7 Days N/mm ²	26.28	27.08	27.18	27.46	
28 Days N/mm ²	43.20	43.60	44.15	44.80	> 42.5

4- Conclusions

This study reports the results of investigation to assess the suitability of basalt and limestone powder to be used as cement raw mix. The strength activity index with Portland cement and the effectiveness of basalt and limestone admixture in controlling alkali-silica reaction were tested according to EN 197-1 Standard ASTM standards. Mortar cubes were specially prepared as per EN 197-1 Standard ASTM standards for these studies using different mixes with varying percentages of basalt and limestone as cement replacement. The results are then compared with EN 197-1 Standard ASTM requirements to assess the suitability of basalt and limestone as cement raw mix.

The clinker cement samples have been changes microstructure reflected by various temperatures which prepared in the furnace of the laboratory. The

finally process of raw mixed proportions and burning in the furnace of the laboratory at about 1450°C produced small balls clinker. These samples clinker represented by Portland cement manufacture can be examined by several analyses such as XRD, XRF, DTA and SEM to identify and studied this clinker basalt.

The principal objective of using alternative materials is to optimize the mix to make best use of available raw materials. A range of calcareous raw materials can be used for cement manufacture, but limestone or chalk predominates. In most cases other calcium-bearing sources do not occur in sufficiently large deposits or amounts to be used as alternatives.

Basalt is the main source of alumina, silica and iron oxides because of its availability and low cost. However, basalt often does not supply the correct chemical balance of constituents and bought in supplements are sometimes required. These may be including silica, iron oxides and alumina. Basalt has a lower alumina to silica ratio than most shales, and also lower alkalis. It is used in some cement plants to add alumina so that higher silica basalt can be utilized.

The following conclusions can be drawn from the experimental results.

- The addition of the basalts material promotes the consumption of free lime and improves the burnability of the raw mix, especially during the final stage of the sintering.
- Despite the slight retarding effect on the hydration process, the added basalt blends improve compressive strength development and do not affect the physical properties of the cements.
- This paper confirmed that the basalt can be used as a resource in cement production and can be used in low cost construction especially in volcanic areas.
- The chemical analysis data of the clinker which formed from basaltic rocks reveal nearly the same oxide composition relatively the chemical analysis of the clinker which formed from claystone except alkalis; chloride and sulphate are abundant more than clinker basalt.
- This paper presents a new beneficial use alternative for basalt material, which is to use basalt material as a feedstock in the conventional manufacture of Portland cement. The paper demonstrates the efficacy of the process at the bench and pilot scales, and presents a summary of practical and economic considerations.
- A pilot scale manufacture was carried out in a batch rotary kiln; X-ray diffraction analysis and EN 197-1 ASTM tests for strength, and setting time suggested that with better optimized burning conditions, basalt material can be successfully incorporated into full scale manufacture.

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